

## SMECTITE FORMATION IN ACID SULFATE ENVIRONMENTS ON MARS

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**Introduction:** Phyllosilicates of the smectite group detected in Noachian and early Hesperian terrains on Mars were hypothesized to form under aqueous conditions that were globally neutral to alkaline. [1]. These pH conditions and the presence of a CO<sub>2</sub>-rich atmosphere should have been favorable for the formation of large carbonate deposits [2]. However, large-scale carbonate deposits have not been detected on Mars. We hypothesized that smectite deposits are consistent with perhaps widespread acidic aqueous conditions that prevented carbonate precipitation.

The objective of our work was to investigate smectite formation under acid sulfate conditions in order to provide insight into the possible geochemical conditions required for smectite formation on Mars. Hydrothermal batch incubation experiments were performed with Mars-analogue, glass-rich, basalt simulant in the presence of sulfuric acid of variable concentration.

**Materials and Methods:** Basalt simulant was prepared by melting reagent-grade oxides and carbonates at 1400 °C in an Au-Pt alloy crucible for 3d under the oxygen fugacity IW+1 and then quenching in water [3]. The final product was ground and sieved to separate out the ≤ 53 µm particle size. For smectite formation experiments, suspensions were prepared in batch reactors (Parr acid digestion vessel) by mixing 250 mg basalt simulant with 15 ml H<sub>2</sub>SO<sub>4</sub> of variable initial concentrations (11.0 ± 0.1 mM, 13.6 ± 0.1 mM, 16.3 ± 0.1 mM, 21.9 ± 0.1 mM, 30.6 ± 0.3 mM and 42.5 ± 0.2 mM). All prepared suspensions were incubated in an oven at 200 °C for 14d. Suspension pH was measured immediately after mixing and at the end of incubation experiments. Basalt simulant after 14 d incubation was examined by X-ray diffraction (XRD), visible and near-infrared reflectance spectroscopy (VNIR) and scanning electron microscopy (SEM) to characterize mineralogy, morphology and composition of the final alteration products.

**Results and Discussion:** The pH measurements revealed that initial suspensions were all acidic with pH ≤ 2 (Fig.1). After 14d of incubation pH (pH<sub>14d</sub>) varied over a wide range from acidic to alkaline (Fig. 1).

The unaltered basalt simulant contained 66 wt% X-ray amorphous glass phase, 32 wt% olivine and 2 wt% chromite [3]. XRD analysis revealed formation of phyllosilicates based on the ~15 Å 001 peak at pH<sub>14d</sub> > 2.2 after 14d incubation (Fig. 2). Smectite was confirmed as the phyllosilicate after treatments with glycerol and KCl and heating to 550 °C. The positions of 02l and 060

diffraction bands indicated formation of the dioctahedral smectite montmorillonite at pH<sub>14d</sub> ~3 and trioctahedral smectite saponite at pH<sub>14d</sub> ~4 and higher (Table 1). Intensity of basaltic glass peak (peak between 20° and 40° 2θ) decreased with respect to unaltered material in smectite-containing samples (Fig. 2) suggesting that glass was transformed into smectite. In addition to smectite, anhydrite precipitated at all values of pH and natroalunite at pH<sub>14d</sub> 1.8 (Fig. 2). XRD analysis also revealed that olivine and chromite were present in all smectite-containing samples, while olivine was dissolved and its XRD peaks disappeared at pH<sub>14d</sub> 1.8 and 2.2.

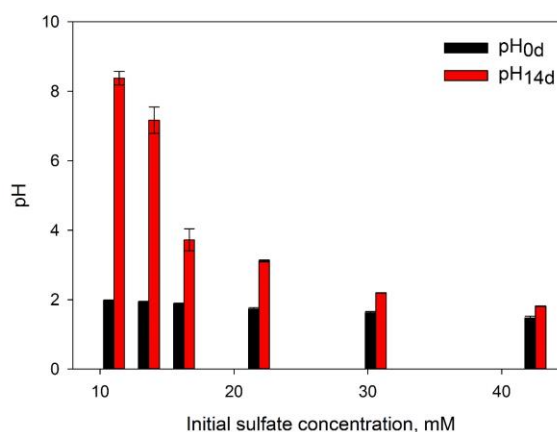


Fig. 1. pH in basalt simulant suspension measured immediately after mixing (0d) and at the end of incubation experiments (14d).

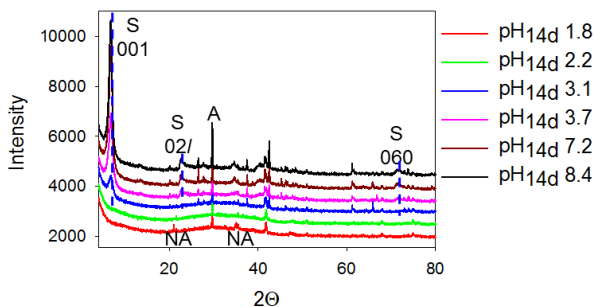


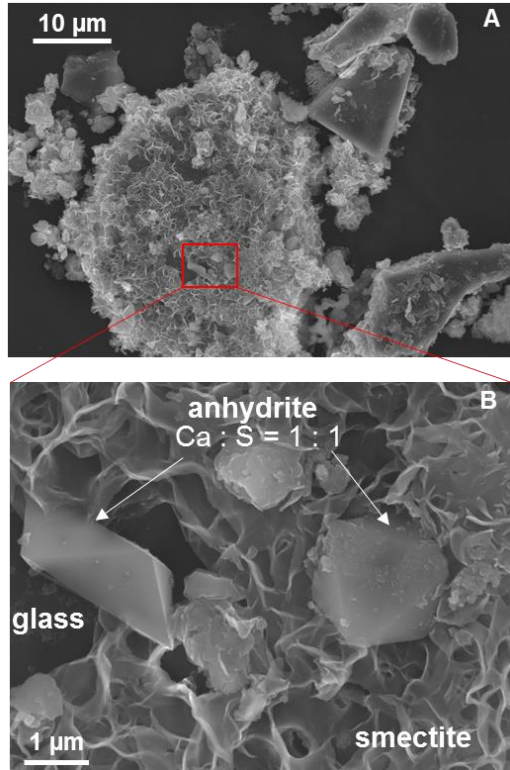
Fig. 2. XRD of basalt simulant after 14d incubation with marked diffraction peaks of alteration products (S- smectite, A- anhydrite, NA- natroalunite). Unmarked sharp peaks correspond to olivine and chromite.

Measurements by VNIR revealed compositional differences in octahedral layer of the synthesized smectite. The spectrum of montmorillonite formed at pH<sub>14d</sub> 3.1 had Al<sub>2</sub>OH band near 2.20  $\mu$ m which is diagnostic of Al-phylosilicates. Saponite formed at pH<sub>14d</sub> 3.7 and 8.4 had Al<sub>2</sub>FeOH band at 2.24  $\mu$ m and (Mg, Fe)<sub>3</sub>OH band at 2.30  $\mu$ m. Saponite observed at pH<sub>14d</sub> 8.4 had a (Mg, Fe)<sub>3</sub>OH band at 2.40  $\mu$ m indicative to formation of Mg-rich saponite.

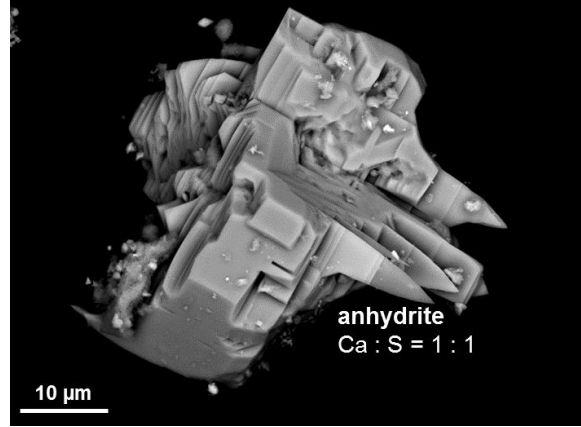
*Table 1. Positions of 02l and 060 diffraction bands of synthesized smectite.*

pH <sub>14d</sub>	Smectite	XRD d-spacing, Å	
		02l	060
3.1	montmorillonite	4.49	1.50
3.7	saponite	4.57	1.53
7.2	saponite	4.58	1.53
8.4	saponite	4.55	1.53

Results of SEM/EDS analyses of the incubated samples showed the glass surface was covered by a “flaky” coating of the smectite associated with ~2  $\mu$ m size anhydrite particles (Fig. 3). In addition, large anhydrite particles (~50  $\mu$ m) were also observed (Fig. 4).



*Fig. 3. (a) SEM image of basalt simulant incubated for 14d at pH<sub>14d</sub> 3.1. Red square area is shown at higher magnification in (b).*



*Fig. 4. SEM image of a large anhydrite particle formed during basalt simulant incubation at pH<sub>14d</sub> 3.1.*

**Conclusions:** Smectite minerals on Mars have been hypothesized to have formed under globally neutral to alkaline conditions during the Noachian and early Hesperian epoch. Our experiments showed that smectite formation through basalt alteration is possible in much more acidic environments suggesting that early Mars could have experienced local and/or perhaps widespread acidic conditions. We found that gradual neutralization of sulfuric acid during basalt weathering led to montmorillonite formation at pH ~3 followed by saponite at pH ~4 and higher. Smectite formed through glass phase alteration and was accompanied by precipitation of calcium sulfate (anhydrite). Similar smectite and sulfate formation under acid sulfate conditions may have occurred in near-surface hydrothermal areas near magma bodies on Mars. Sulfur dioxide (SO<sub>2</sub>) degassing from volcanic processes is a potential source of acidity development during smectite formation

**References:** [1] Bibring, J.-P. et al. (2006) *Science*, 312, 400-404; [2] Fairén, A. G. et al. (2004) *Nature*, 431, 423-426; [3] Peretyazhko et al. (2016) *Geochimica et Cosmochimica Acta* 173, 37-49.